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STUDY OF THE OXYGEN ROLE IN THE PHOTOLUMINESCENCE OF ERBIUM DOPED NANOCRYSTALLINE SILICON EMBEDDED IN A SILICON AMORPHOUS MATRIX

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Abstract

We have produced and studied erbium doped nanocrystalline silicon thin films with different oxygen and hydrogen content in order to evaluate the influence of the matrix on the Er^{3+} emission and on the 0.89 eV and 1.17 eV bands. Films were grown by reactive magnetron sputtering on glass substrates under several different conditions (RF power, Er content and gas mixture composition) in order to obtain different microstructures. The structural parameters and the chemical composition of the samples were obtained by X-ray in the grazing incidence geometry, Raman spectroscopy and Rutherford back scattering analysis. Using X-ray technique combined with Raman spectroscopy information on the crystalline fraction and the average crystallite size of Si nanocrystals was obtained. Dependence of the 0.89 eV and 1.17 eV peaks in Si heterogeneous matrixes on the films crystallinity and O/H ratio has been analyzed.

Keywords: nc-Si, erbium-doping, optical properties, thin films.

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1. Introduction

The long awaited silicon based optoelectronics may become reality owing to the new properties of nanostructures, which show quantum confinement. Recently, silicon thin films with crystalline nano-regions (nanocrystals, NC's), of typical size <10*nm*, have attracted researcher's interest. Special efforts are also placed on the possibility to use the low-dimensional structures as the basic materials for rare earth doping. Among rare earth elements, erbium takes special significance for optical communication

systems due to the emission line at 1.54 μm (that originates by the intra-4f transitions of Er^{3+} ions) [1-4].

Our aim is to obtain stable 1.54 μm room temperature PL from Er-doped nc-Si films. With this work we want to clarify the matrix effect, based on the erbium, oxygen and hydrogen amount, on this stabilization, for that we describe the results of photoluminescence studies carried out for the nc-Si:Er films in the near IR range and discuss the role of Si nanocrystalline fraction and of the oxygen-to hydrogen ratio, O/H incorporated into films in the luminescent properties.

2. Experimental

Nanocrystalline silicon thin films doped with erbium were grown by the RF magnetron sputtering method in Ar/H_2 atmosphere on ordinary glass substrates [5]. We grew erbium doped silicon thin films that differ mainly in the amount of oxygen and hydrogen incorporated into the films and in structure (nanocrystalline size and crystalline fraction). The samples had different O/H incorporated ratio varying from 0.6 to 9, this different O/H content have a big impact on the film microstructure and consequently on their properties.

The chemical composition (see Table 1) was determined by combining Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) techniques. Structural characterization was evaluated by the conventional techniques as grazing X-ray diffraction and micro-Raman spectroscopy under excitation with 514.5 nm line of Ar^+ laser. To determine the size and volume fraction of crystallites computer simulations were used to the Raman spectra, considering the spectral profile as a superposition of the amorphous and crystalline components. The crystalline profile was calculated on the basis of the Strong Phonon Confinement model [6] and a Gaussian profile was attributed to the amorphous TO peak.

Table 1 : Growth conditions for erbium doped nanocrystalline silicon thin films, their atomic content and structural parameters

Sample	Temperature (ºC)	RF power (W)	Er (at%)	Si (at%)	O (at%)	H (at%)	D_R (nm)	C_R (%)
P11	300	80	1.4	85.6	10	3	7.8	55
P7	300	40	2.8	75	20	2.2	7.2	34
Er56	200	80	2.3	85	4.7	8	0	0
Er48	200	40	3	81	14	3	6.6	39

D_R - Average crystal size by Raman; C_R- crystalline volume fraction by Raman

Photoluminescence (PL) measurements in the infrared spectral region were performed with the Brucker 66V Fourier-transform spectrometer. The signal was detected by North-Coast germanium detector; model EO-817, being excited by the 514.5 nm line of an Ar^+ laser. The samples were studied in the temperature range of 6 – 160 K. For the visible spectra the samples were excited with the He-Cd laser and the signal detected with a cooled photomultiplier tube.

3 – Results and discussion

The results of the chemical and structural characterization are presented in Table 1. The RBS results indicate that there are samples with more oxygen than hydrogen (P11, P7 and Er48) and one sample with more hydrogen than oxygen (Er56). The erbium content in the samples varies from 1.4 at% (for P11) to 3 at% (for Er48).

Figure 1 shows the Raman (a) and the XRD (b) spectra of some typical samples. All samples shows in the Raman spectra the broad band at 480 cm^{-1} due to the silicon amorphous matrix. The Er56 sample does not show any crystalline peak in the Raman spectra neither in the XRD pattern. In contrast, the diffraction peaks of c-Si (111) at $2\theta \approx 28.4^o$, (200) at $2\theta \approx 47.3^o$ and (311) at $2\theta \approx 56.1^o$ are seen for all other samples, which also show the transverse optical (TO) mode of c-Si around 520 cm^{-1} in the Raman spectra.

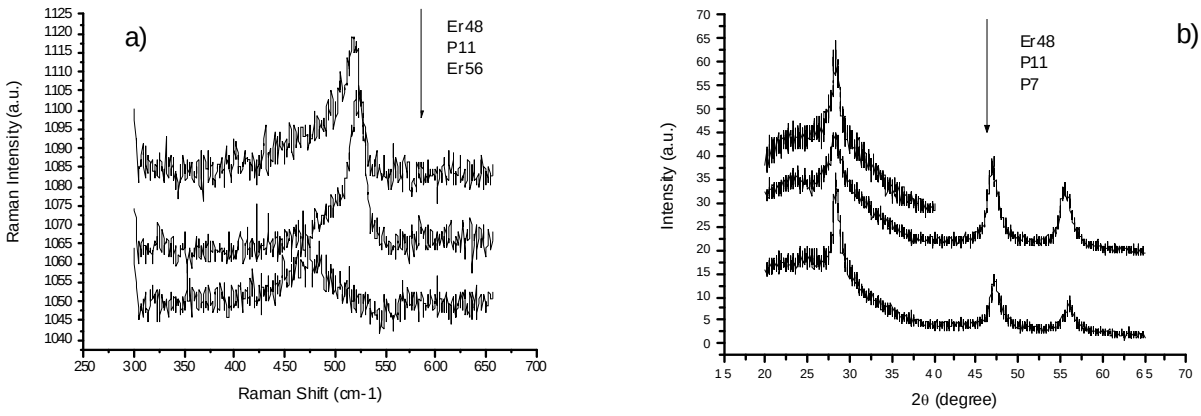

Figure 1: (a) Raman and (b) XRD spectra of some typical nc-Si:Er thin films.

The Raman and XRD studies separates these samples in two groups, one of basically amorphous samples and the other group contain samples with an average crystal size of approximately 7.0 nm and a volume fraction of crystallites ranging from 34% to 55% (see table 1).

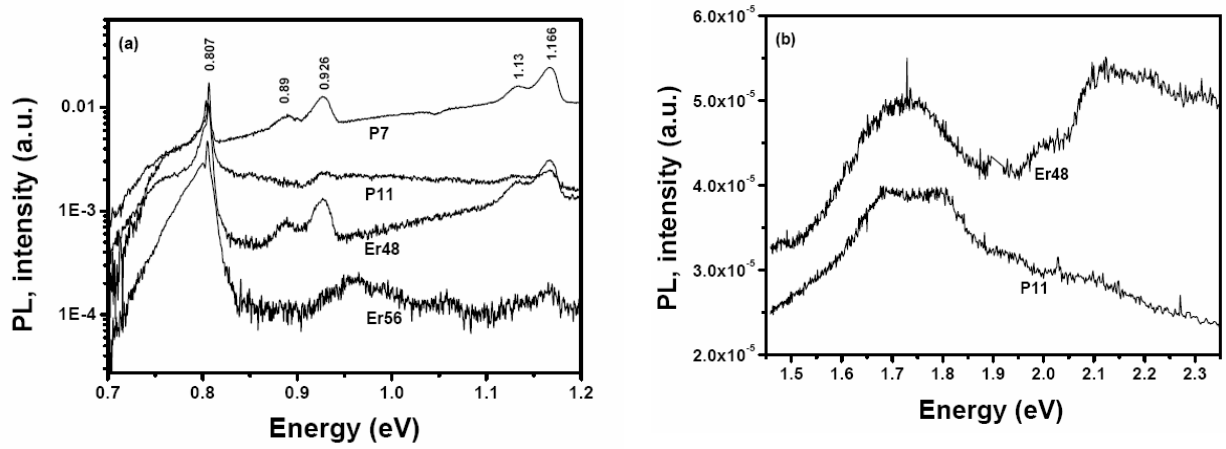

Figure 2: 12K PL spectra in the infrared (a) and visible (b) spectral range for the studied samples.

Figure 2 shows the low temperature near IR and visible PL spectra of the erbium doped silicon films with different crystallinity and crystallite size, as determined by Raman data (reported in Table 1).

It is observed in figure 2 a) that in all the studied samples the PL peak assigned to the intra-4f transition of Er^{3+} (intra-atomic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of Er ions) is present. Differences can be seen in the details of the PL features in the spectral range 0.85-1.2 eV, and also in the PL in the visible range, namely in the green-yellow spectral range. In particular the PL peak at 0.89 eV is only present in the P7 and Er48 samples. According to our previous work based on spectroscopic ellipsometry studies (SE) [7], the dopant concentration needed for obtaining the characteristic Er^{3+} emission is lower than 0.03 at% and the excess of erbium incorporated into the films does not form Er metallic clusters but rather $ErSi_2$ or Er_2O_3 compounds. In particular, $ErSi_2$ has been found in the P7 and Er48 samples, which have approximately 3% of Er, while Er_2O_3 has been found in the P11 and Er56 samples with lower Er%. Our results also indicate a competition between Si and Er to get oxygen forming SiO and Er_2O_3, respectively. The details of the PL features (see figure 2) seem to support the existence of different sites for Er related to a different film microstructure and matrix. Indeed,

according to the different PL characteristics observed in figure 2, samples can be grouped into two categories, namely P7 and Er48 have similar IR and visible PL spectra, which differ from that of P11 and Er56 samples. In analogy with the crystalline silicon, the PL lines at 0.89 and 0.926 eV could be related with dislocations in nanocrystals [8]. Furthermore, in crystalline silicon, it is well known that the PL lines at ≈ 1.13 and ≈ 1.17 eV are described as the exciton- related PL bands appearing in the large diameter crystallites. As shown in figure 2, these lines are different for the P7 and Er48 and for the P11 and Er56 groups of samples.

From the structural point of view (based on Raman and X-ray) only the sample Er56 does not show the presence of large silicon crystals. Therefore, these PL features cannot be explained by the presence or not of crystallites. Rather, we might relate the PL features with the chemical composition of the matrix, and specifically the different sites for Er. From the compositional point of view, the samples with an O/H ratio > 4 have a well pronounced 0.926 eV and 1.17 eV peaks and the samples with O/H ratio < 3 have a less pronounced structure. In particular, the P7 and Er48 samples with Er bounded to silicon forming $ErSi_2$ [7] and with a similar volume fraction of crystallites embedded in a SiO matrix have similar PL spectra. Similarly, the P11 and Er56 samples with erbium bounded to oxygen, forming Er_2O_3 and a large fraction of crystallites in a SiO matrix also show similar PL spectra features.

More inside in the PL features was made analyzing the temperature effect on these structures. Figure 3 shows the temperature behavior of the PL for the P11 and P7 samples. It is visible that the intensity of the PL bands at 0.89 eV, 0.926 eV, 1.13 eV and 1.166 eV, comparing with the intensity of Er^{3+} PL band, are quite different in the two samples. For P7 sample these lines are very intense, in opposite to the P11 sample, indicating that the content of the defects that originate the optical centers are different in both samples. While the 0.926 eV, 1.13 eV and 1.166 eV can be observed in both samples it must be mentioned that the 0.89 eV band is only detected for P7 and P48 samples suggesting that this band could be related with the presence of $ErSi_2$. If there is the case and despite the appearance of the new optical features it is interesting to note that the Er quenching mechanisms is independent of the chemical composition of the matrix as shown in inset of figure 3(a) where the temperature dependence of Er^{3+} integrated intensity is shown for both P7 and P11 samples.

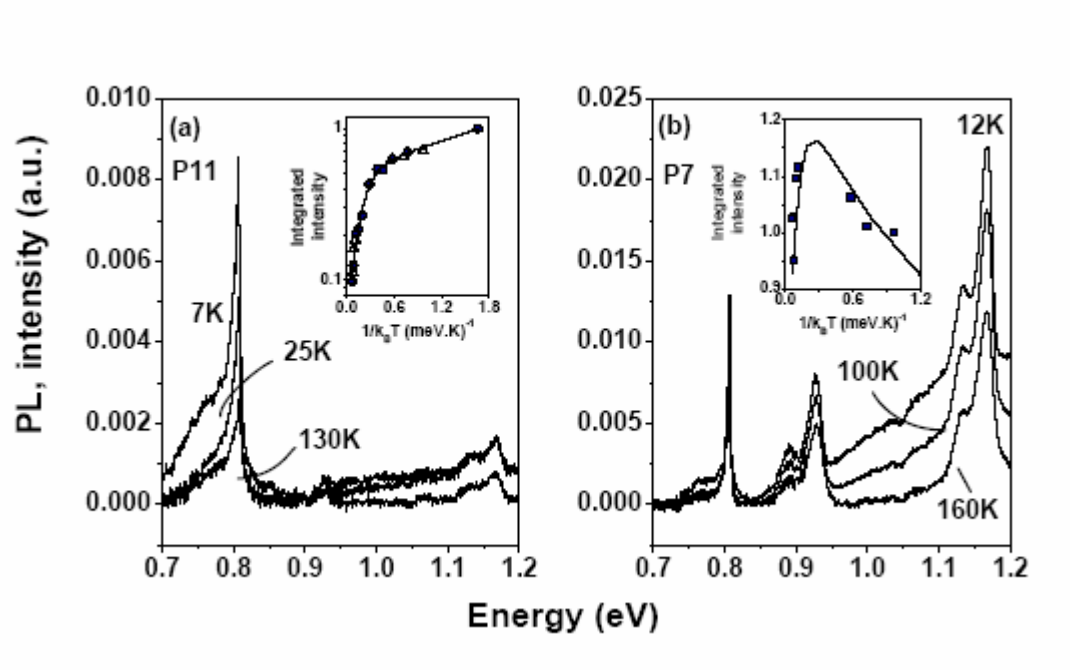

Figure 3 – Temperature dependent PL spectra for samples P11 (a) and P7 (b). Inset of fig(a): integrated intensity temperature dependence of Er-related PL for P11 (triangles) and P7 (circles) samples. The best fit was obtained considering the activation energies described in text. Inset of fig(b): integrated intensity temperature dependence of the 0.89 eV peak.

The quenching processes are well described by two activation energies of E_1=1.25±0.73 meV and E_2=13±2.7 meV. Although the intensity of the PL bands at 0.926 eV, 1.13 eV and 1.166 eV practically keeps constant during the studied temperature range suggesting that these lines are related with dislocations, the integrated intensity of the 0.89 eV transition is well described by a thermally population from the Er^{3+} related center (see the inset of figure 3(b)) as observed by the its intensity increase assuming that is the decay path of Er^{3+} with E_1= 1.25 meV that populates the 0.89 eV centre while the decrease in intensity undergoes the same quenching process of Er^{3+} with E_2=13 meV.

4. Conclusions

We have studied the dependence of the PL bands around 0.89 eV and 1.17 eV on the films nanocrystallinity and O/H ratio in Er-doped nanocrystalline thin films. It has been shown that the intensity of these PL bands is strongly different depending on the chemical composition of the matrix as also the intensity of these PL lines present a slower thermal quenching (less than 10% from 7K to 160K) as compared with the Er^{3+} behavior (around 85% in the same temperature range). The intensity

of the PL bands at 0.926 eV, 1.13 eV and 1.166 eV practically keeps constant during the studied temperature range suggesting that these lines are related with dislocations. Otherwise the intensity of the PL band at 0.89 eV, only visible in the two samples containing $ErSi_2$, is well described by a thermally population from the Er^{3+} related center. It has been verified that Er quenching mechanisms is independent of the chemical composition of the matrix.

The studies carried out indicate that there exist a correlation between the matrix composition and the PL features of nc-Si:Er films in the near infrared range, where the results seem to be related with the existence of different sites for Er as $ErSi_2$ or Er_2O_3 compounds in nanocrystalline films.

Acknowledgment

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